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Semiconducting Properties of Cu_5SbO_6

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Thermoelectric power, electrical resistivity, I - V characteristics, relative electrical permittivity, dc magnetization and ac magnetic susceptibility measurements carried out on Cu_5SbO_6 showed p -type semiconducting behaviour with the activation energy of 0.24 eV as well as ferrimagnetic order with the Néel temperature of 5.2 K. The effective magnetic moment of $5.857 \mu_{\text{B}}/\text{f.u.}$ revealed the orbital contribution to the magnetic moment. Large value of the relative electrical permittivity indicated that the Cu^{2+} ions with the unscreened and unfilled electron shells are responsible for the polarizability and forming of electric dipoles.

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1. Introduction

The compound with the chemical formula Cu_5SbO_6 is known to exist in the Cu-Sb-O system [1–4]. Cu_5SbO_6 is interesting in the context of geometric frustration [5] and the Jahn-Teller distortion for $3d^9 \text{Cu}^{2+}$ which frequently prevents the formation of ideal magnetic lattice geometries [6]. In general, compounds based on Cu^{2+} ions are especially appealing because at spin 1/2, quantum effects are expected to be important in determining the magnetic properties [6]. The crystal structure of Cu_5SbO_6 in its ordered stacking phase was found from the structure refinements to be monoclinic, $C2/c$ space group (No. 15), with unit cell parameters at 300 K: $a = 8.92346(3)$ Å, $b = 5.592776(16)$ Å, $c = 11.84459(4)$ Å, and $\beta = 103.58453(17)^\circ$ [6]. This structure can be described as a modified Delafossite structure, in which the layers of ordered edge sharing Cu^{2+}O_6 and Sb^{5+}O_6 octahedra are formed, while the Cu^+ are incorporated between these planes, giving very interesting the mixed-valence system [7]. The magnetic susceptibility measurements of $\text{Cu}(\text{I})_3\text{Cu}(\text{II})_2\text{Sb}(\text{V})\text{O}_6$ between 5 and 300 K indicated the presence of a singlet-triplet spin gap of 189 K [6], i.e. of 0.016 eV.

This paper reports on electrical properties, which have not previously been reported and magnetic ones for comparison with others presented in Ref. [6].

2. Experimental details

Cu_5SbO_6 was obtained by the conventional solid-state reaction technique using the starting mixture of oxides containing CuO and $\alpha\text{-Sb}_2\text{O}_4$ in molar ratio 10:1.

The mixing of the calculated amount of oxides was heated in several stages at temperatures not exceeding 950 °C. Only a set of lines characteristic for Cu_5SbO_6 was recorded in the diffraction pattern (XRD) of the sample after last heating stage.

The electrical conductivity σ has been measured with the aid of the four-probe dc method in the temperature range 280–520 K using the HP 34401 A digital multimeters controlled by a computer using LabView[®] commands. The I - V characteristics were measured at 300 K and at 400 K. The thermoelectric power (TEP) was measured in the temperature range 280–520 K with the aid of a differential method using a temperature gradient ΔT of about 5 K. Dielectric measurements were carried out using pellets, polished and sputtered with (≈ 80 nm) Ag electrodes in a frequency range from 10^1 to 10^6 Hz applying a Novocontrol Alpha Impedance Analyzer. For electrical measurements, the powdered samples were compacted in disc form (10 mm in diameter and 1–2 mm thick) using pressure of 1.5 GPa, and next they were sintered at 473 K for 2 h. Dynamic (ac) magnetic susceptibility was measured with the aid of a Quantum Design System (MPMS XL) and recorded in the temperature range 2–300 K and at an internal oscillating magnetic field $H_{\text{ac}} = 3.9$ Oe with an internal frequency $f = 300$ Hz. Magnetization isotherm was measured at 4.2 K in the static (dc) magnetic field up to 70 kOe.

3. Results and discussion

Thermoelectric power and electrical conductivity measurements of Cu_5SbO_6 in Fig. 1 showed the p -type semiconducting properties in the temperature range 280–

520 K. A thermally activated conduction of the Arrhenius type with the activation energy of 0.24 eV as well as the linear temperature dependence of thermoelectric power were observed. It seems natural that the divalent Cu atoms and the holes coming from the 3d configuration of Cu^{2+} ions are responsible for the p -type conduction. This measurement well correlates with the fact that the spin $1/2$ Cu^{2+} ions form dimers in the honeycomb layer [1]. Independently of temperature the I - V characteristics in Fig. 2 revealed the ohmic region. The values of the amperage at 100 V are equal to 0.52×10^{-4} A at 300 K and 5.31×10^{-4} A at 400 K. The broadband dielectric spectroscopy in Fig. 3 showed the strong increase of relative permittivity ϵ_r with increasing temperature, especially for low frequencies. In the same time the maximum of energy losses evidenced by the $\tan \delta$ (inset of Fig. 3) shifts towards both the higher temperatures and frequencies. It suggests that the Cu^{2+} ions with the unscreened and unfilled electron shells are susceptible on polarizability and forming of electric dipoles.

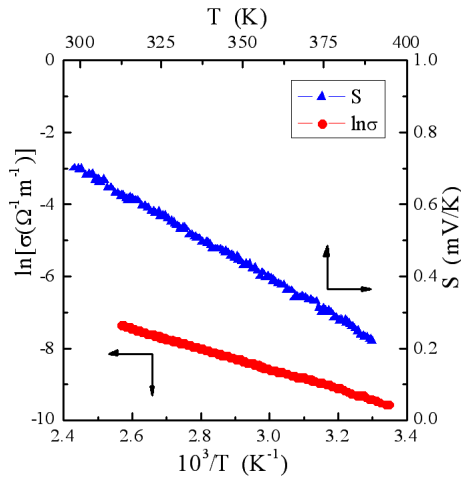


Fig. 1. Electrical conductivity $\ln \sigma$ vs. reciprocal temperature $10^3/T$ and thermopower S vs. temperature T .

The grow of ϵ_r on increasing temperature and/or decreasing frequency was observed in some ferroelectric materials and can result from the Maxwell-Wagner-type effect (MW) [8–11]. MW relaxations are non-intrinsic and can be described by an equivalent electric circuit consisting of the bulk contribution from the sample, connected in series to a parallel RC -circuit with R and C being much higher than the corresponding bulk quantities. This region with high resistance in the sample can arise from insulating depletion layers at the metal-to-sample contacts or other type of internal barriers. At high frequencies and/or low temperatures, the layer capacitance becomes shortened and only bulk behaviour is detected. However, with increasing temperature and/or decreasing frequency, the high capacitance of these insulating layers leads to the detection of markedly growing value of ϵ_r [11].

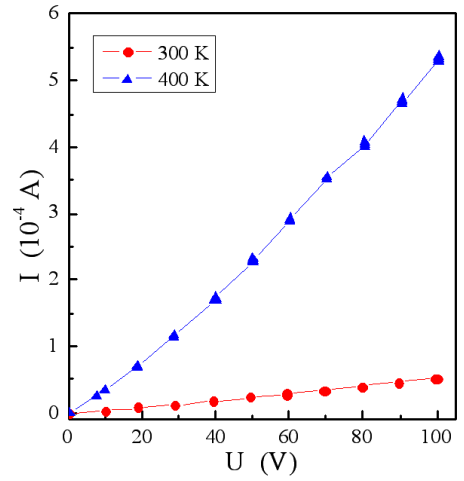


Fig. 2. The I - V characteristics at 300 K and 400 K.

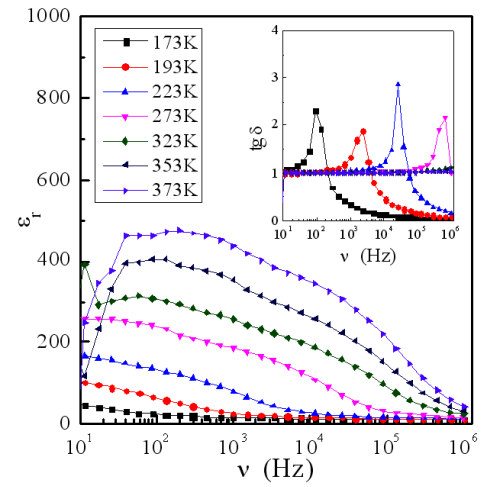


Fig. 3. Relative permittivity ϵ_r and loss tangent $\tan \delta$ (inset) with frequency ν at 173, 193, 223, 273, 323, 353, and 373 K.

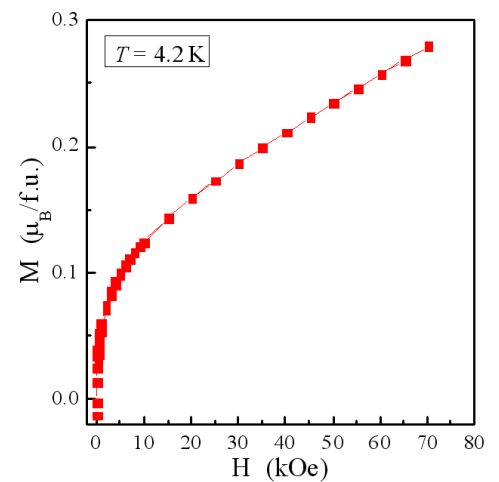


Fig. 4. Magnetization M vs. magnetic field H at 4.2 K.

The magnetization isotherm measured at 4.2 K (Fig. 4) and the inverse susceptibility vs. temperature (Fig. 5) indicate the ferrimagnetic order in Cu_5SbO_6 with the ferrimagnetic Néel temperature $T_N = 5.2$ K (inset of Fig. 5) and the paramagnetic Curie–Weiss temperature $\theta = -80$ K. The experimental effective magnetic moment was estimated from equation: $\mu_{\text{eff}} = 2.83\sqrt{C}$, where C is the molar Curie constant. For $C = 4.283$, taken from experiment, we have $\mu_{\text{eff}} = 5.857 \mu_B/\text{f.u.}$ This value is quite close to the theoretical one which was calculated from equation $p_{\text{eff}} = \sqrt{2}p$, where $p = g\sqrt{J(J+1)}$ is the effective number of the Bohr magnetons [12], $J = 5/2$ is the effective angular momentum and $g = 6/5$ is the Landé factor for the Cu^{2+} ion. It means that the orbital contribution to the magnetic moment, caused by the Jahn–Teller distortion for $3d^9 \text{Cu}^{2+}$ [6], takes place in this case.

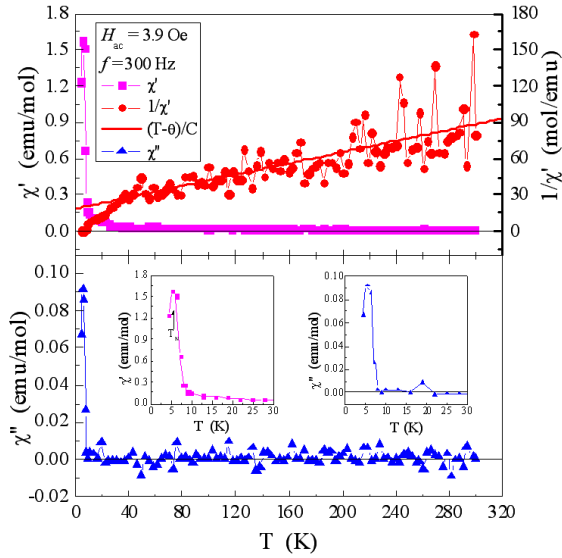


Fig. 5. In phase χ' and $1/\chi'$ as well as out of phase χ'' components of zero field fundamental susceptibility vs. temperature T recorded at $H_{\text{ac}} = 3.9$ Oe with $f = 300$ Hz. The solid (red) line indicates a Curie–Weiss behavior. Inset: χ' and χ'' enlarged below 30 K show the ferrimagnetic Néel temperature $T_N = 5.2$ K and the energy loss, respectively.

The imaginary component χ'' of magnetic susceptibility in Fig. 5 is close to zero above 5.2 K, i.e. in the Curie–Weiss region. No magnetic interactions or spin fluctuations are present.

4. Conclusions

Electrical measurements of Cu_5SbO_6 showed p -type semiconducting behaviour with the activation energy of 0.24 eV and ohmic region both at 300 K and 400 K. The strong increase of relative permittivity with increasing temperature seems to be connected with the Cu^{2+} ions, which have the unscreened and unfilled electron shells. These ions are susceptible on polarizability and forming of electric dipoles. The magnetic measurements indicated the ferrimagnetic order with $T_N = 5.2$ K and without no extremes at 25 K and at 120 K, which were observed in Ref. [6] above T_N on the magnetic susceptibility curve in the applied magnetic field of 0.5 T.

Acknowledgments

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